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Development of Sputtered High Temperature Coatings for Thrust Chambers

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ABSTRACT

Adherent insulating coatings were developed for thrust chamber service. The coatings consisted of nickel and a ceramic, and were graded in composition from pure nickel at the thrust chamber wall to pure ceramic at the coating surface. The coatings were deposited by rf sputtering from a target with a reversed composition gradient, which was produced by plasma spraying powder mixtures. The effect of deposition parameters on coating characteristics and adherence is discussed.

INTRODUCTION

BACKGROUND

Presently planned hydrogen-oxygen thrust chambers consist of an inner wall surrounded by cooling channels cut in an outer containment structure. The inner wall is subject to the coolant temperature (boiling liquid hydrogen) on its outer surface and the flame temperature on its inner surface. These temperatures, together with the cyclic nature of the thrust chamber service, limit the useful life of the inner wall. It is therefore desired to reduce the temperature extreme by the application of a thermally insulating coating on the inner surface.

The problem of maintaining adherence of a thermally insulating coating to a metal substrate through wide temperature variations is viewed mainly as one of accommodation of the strain generated by the difference in the product of the thermal expansion coefficient and temperature between the metal substrate and the coating, combined with thermal shock of start-up. In addition, the thermal gradient through the coating must not be so large as to produce length changes on opposite sides of the coating in excess of its ability to deform, either elastically or plastically, without spallation. Cracking of the insulating layer may be permissible if it remains bonded to the substrate. Another consideration is that the thickness, thermal conductivity, and configuration of the insulating coating must also be such that no part of the insulating coating was subjected to temperatures in excess of its melting point.

OBJECTIVE

The overall objective of this work was to demonstrate that the desired thermally insulating coating could be achieved through utilization of a graded composition interlayer between the metal substrate and a ZrO_2 or Al_2O_3 ceramic layer. The grading was intended to accommodate the strains generated in service by the thermal expansion mismatch between metal substrate and ceramic. The thickness and profile of the graded composition layer were considered experimental variables.

The objective of work in Task I was to determine the coating specification and values of deposition parameters favorable to maximum adherence of the insulating coating and, to qualitatively establish the adherence achieved by thermal cycling and thermal shock tests. The object of Task II was to coat two NASA spool pieces according to the results of Task I work, and provide them to NASA for firing tests.

TECHNICAL ACCOMPLISHMENTS

TASK I

Experimental Procedure

The sputtering apparatus designed for this project was of the triode or supported discharge type. The general arrangement is shown in Figure 1. The spool piece to be coated was utilized as part of the chamber wall. The hardware shown was mounted on a standard BNW base assembly containing the electron source, power and cooling water connections, and the pumpout port.

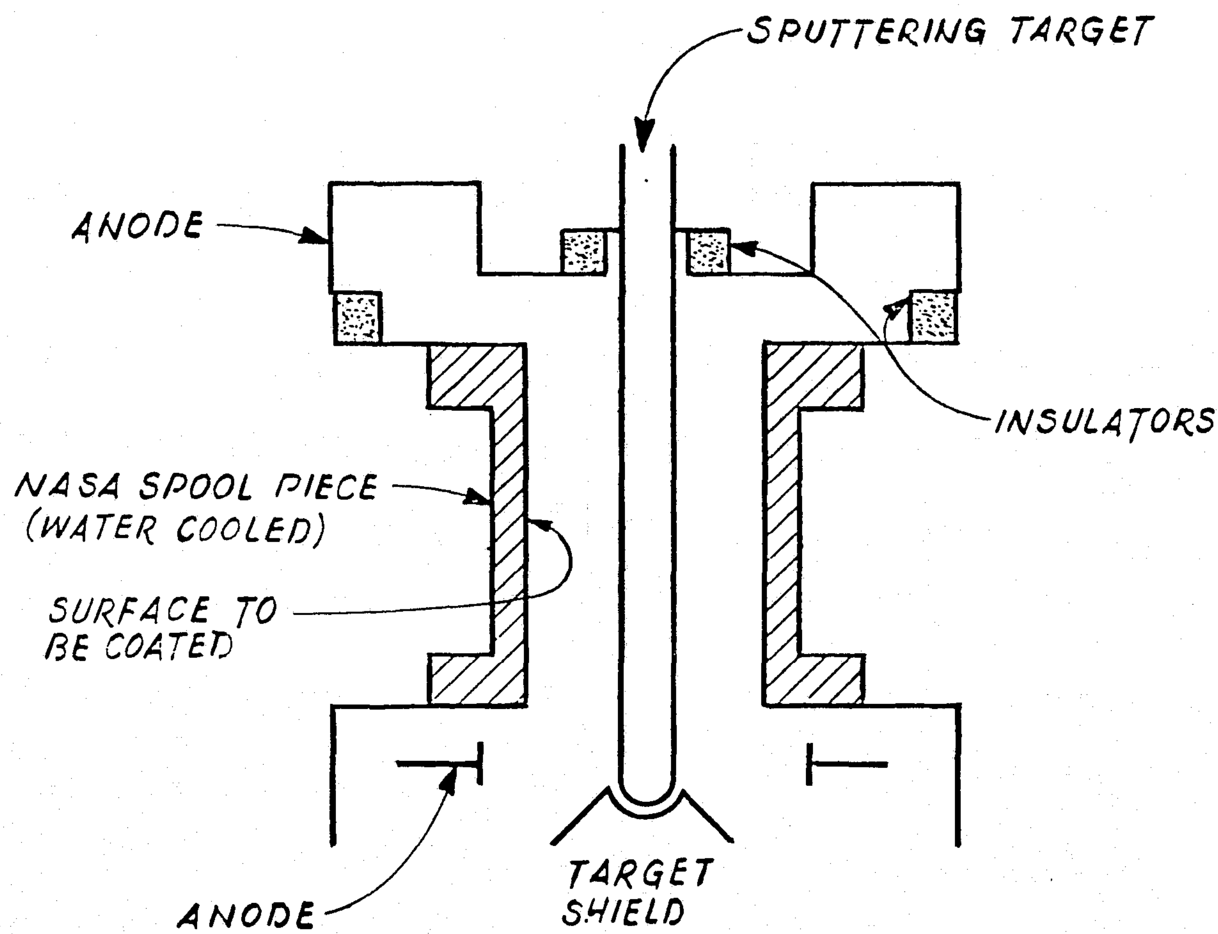


FIGURE 1. Sputtering Hardware Arrangement for Spool Piece Coating.

The centrally located target, or source of the material to be deposited, is shown in cross-section in Figure 2. The target was fabricated by plasma spraying thin layers of mixed metal and ceramic powders. The mixtures ranged from 100% ceramic to 100% nickel by 20% (volume) increments, and were sprayed in the indicated order so that the reverse gradient would be formed on the substrate during sputtering.

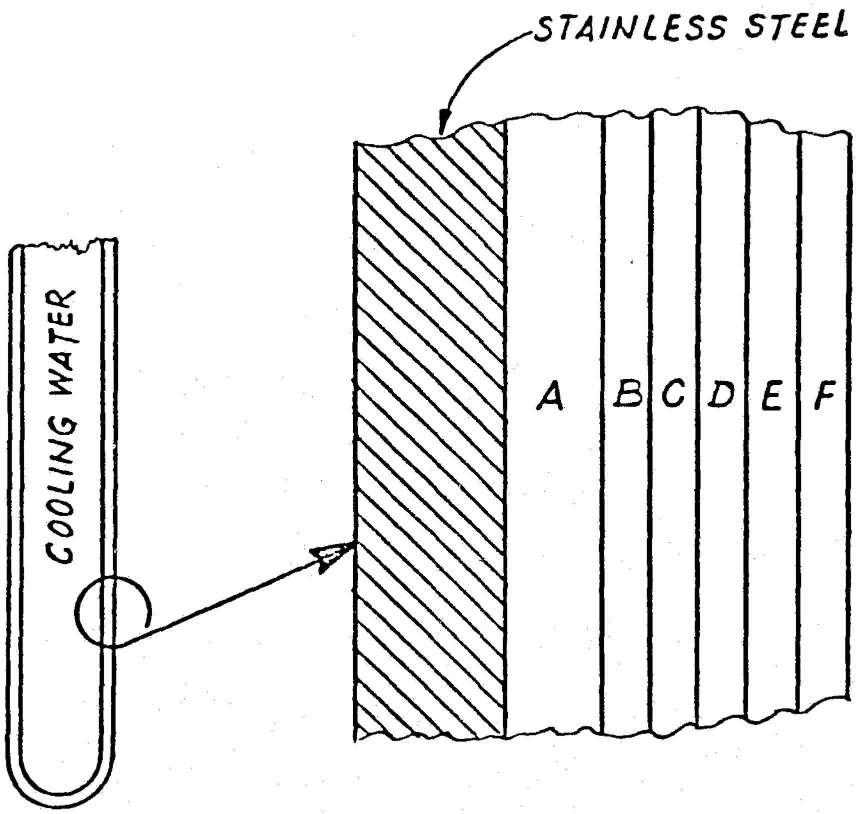
The following ceramics were investigated:

- Zirconia stabilized with 5% calcia
- Zirconia stabilzed with 8% yttria
- Magnesium zirconate
- Alumina

In each case nickel was used as the grading element.

For the experimental depositions of Task I, the substrate was a 2 mm thick copper liner placed inside the NASA spool piece. The liner was used to permit destructive evaluation of the coating by thermal cycling, and also sectioning for metallography, etc.

In the deposits made for inhouse evaluation, the substrate was cooled by contact with the spool piece, which was cooled by flowing warm water (60^{o}C). The actual substrate temperature was not measured, and depended on the degree of contact, cleanliness of the contacting surfaces, etc. The coatings for shipment to NASA LeRC were deposited directly on the cooled spool pieces; in this case the temperature is known to be within a few degrees of the water temperature.



A —	100%	CERAMIC	
B —	80%	CERAMIC	20% NICKEL
C —	60%	CERAMIC	40% NICKEL
D —	40%	CERAMIC	60% NICKEL
E —	20%	CERAMIC	80% NICKEL
F			100% NICKEL

FIGURE 2. Layering of Target Materials on Stainless Steel Target Support. Layer Thickness 0.003" except Layer "A" 0.006".

Sputter Deposition

Depositions performed during the program are summarized in Table I and discussed below. In the table, the oxygen partial pressure is quoted in qualitative terms because of the difficulty of making meaningful measurements in an operating sputtering system. The difficulty is due to the rate of gettering being about equal to the rate of oxygen introduction. The oxygen flow rates used in the above experiments produced oxygen partial pressures of 3 to 9 x 10^{-5} torr when the sputtering system was shut down; however no oxygen peak was detectable when the system was operating.

Depositions 1 and 2 were made primarily to determine the suitability of the target configuration and to measure the sputtering yield. The main concern was that the reverse graded sprayed material might have inadequate thermal shock resistance to withstand the application of the desired power density of 10-20 watts/cm^2. The targets performed satisfactorily; however a nonuniform erosion profile was observed.

Deposition 3 consisted of manipulation of available sputtering parameters to obtain a uniform erosion profile. The voltages on the two anodes were varied until a satisfactory balance in plasma currents was obtained. The success of this technique was indicated by the uniform erosion profile obtained in subsequent depositions.

TABLE I

Deposition Experiments

Number	Ceramic Deposited	rf Power (watts)	Thickness (mils)	Density (g/cc)	Resistance (ohms)	Comments
1	$ZrO_2(CaO)$	370	0.3	NM	0	Target test
2	$ZrO_2(CaO)$	1000	3.5	NM	0	" "
3	Direct current experiment for uniform erosion profile.					
4	ZrO_2 (CaO)	1500	4.1	8.07	0	Overcoated with stainless steel
5	ZrO_2 (CaO)	1500	2.5	6.29	NM	High oxygen (deposit flaked)
6	ZrO_2 (CaO)	1500	2.9	6.14	NM	Medium oxygen (deposit flaked)
7	ZrO_2 (CaO)	1350	3.9	8.29	0	Thermal cycling and shock tests
8	ZrO_2 (Y_2O_3)	1350	2.4	8.70	2.5	Thermal cycling and shock tests
9	Al_2O_3	1350	2.9	8.41	100	Thermal cycling and shock tests
10[1]	MgO/ZrO_2	1350	3.5	8.41	700	Spool piece 13[2]
11[1]	Al_2O_3	1350	3.6	NM	18K	Spool piece 20
12[1]	MgO/ZrO_2	1350	3.0	NM	> 2M	Spool piece 21

(1) These depositions were on NASA spool pieces. The inside wall was prepared by bead blasting to provide a uniformly roughened surface, rinsed with solvent, and ion etched to an integrated intensity of 20 ma-min/cm^2.

(2) Not intended for shipment; spool piece did not meet dimensional requirements.

Depositions 4 through 6 employed a sheet copper substrate wrapped into a cylinder which was a snug fit in the spool piece. These depositions differed primarily in the partial pressure of oxygen added to the krypton sputtering atmosphere. It was found that, at the high power level used (17 watt/cm^2) and with no added oxygen, the deposit was electrically conductive, indicating a strong oxygen deficiency. The two levels of added oxygen investigated however, resulted in flaking of the deposit, a nonuniform erosion profile of the target, and difficult operation of the sputtering system, particularly with respect to plasma instability and excessive arcing.

Examination of the coated substrates from these depositions suggested that they had been exposed to high temperatures in spite of their nominal contact with the water cooled spool piece. The experiments also indicated that the system would not operate in a satisfactory manner with a partial pressure of oxygen sufficient to produce an insulating deposit. Previous experience with ceramics sputtered in similar apparatus indicated that: a) insulating deposits could be obtained at low substrate temperatures, and b) the apparatus would tolerate a higher level of oxygen if operated at reduced power levels (particularly with added oxygen). Therefore, the next set of four depositions (7, 8, 9 and 10) were planned around the following features:

1) A tubular copper substrate machined to a tight fit in the spool piece, and with a thick enough wall that it would not buckle inward when heated. This was to ensure a low substrate temperature.

2) A target power-time profile as shown in Figure 3, where the power is progressively decreased as the ceramic content of the material being sputtered increases. This was to ensure that the pure and nearly pure ceramic were deposited at a reduced rate.

3) Coincident with the reduced power, increase the oxygen partial pressure within the operational limits of the apparatus. This was to aid in achieving insulating behavior in the ceramic.

4) A second set of targets with thinner sprayed layers was utilized, since the previous coatings were thicker than expected, primarily due to low density. (Note: With a graded target the deposit thickness cannot be controlled in the usual manner without affecting the deposit composition limits).

The set of four experiments utilized the four ceramics previously listed. All other deposition parameters were held constant.

The sputtering yield for each material was estimated from previous experiments, and used to establish the watt-hours to be applied to the target. The goal was

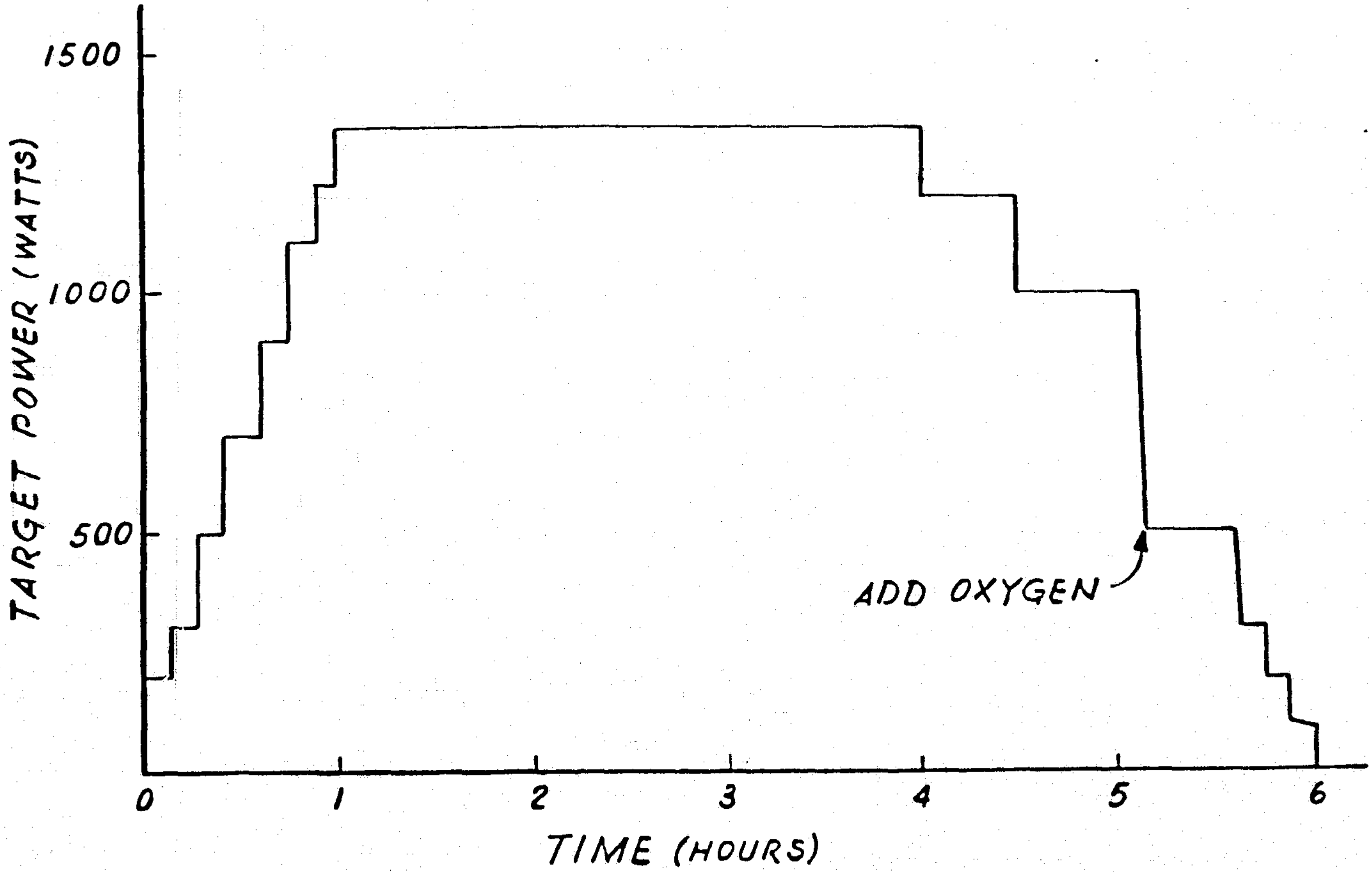


FIGURE 3. Typical Deposition Power Profile.

to completely remove all the graded material and about one-half of the pure ceramic layer. The watt-hour product was always conservative, since it was considered better to have a coating which did not reach pure ceramic than one which was overcoated with the target support material.

Evaluation

Electrical Conductivity

The deposits from these experiments were adherent, smooth-surfaced, and grey-black in color. They exhibited various levels of electrical conductivity which was determined by the degree of approach to the pure ceramic, which in turn was determined by the accuracy of the sputtering yield estimate used to establish the duration of the deposition.

Thermal Cycling and Shock

The coated substrates from depositions 7, 8, and 9 were subjected to progressively more severe thermal cycles and thermal shock treatments described in Table II. A ring about 0.5 inch wide was removed from each substrate by abrasive sawing and tested as a complete ring. No spalling or debonding was observed in any of the tests.

In part, these results were due to the incomplete approach to pure ceramic and/or the small thickness

TABLE II

Thermal Cycling and Shock Tests

1. Slowly cool from room temperature to liquid nitrogen temperature and warm up in air; one cycle.

2. As for (1), except rapid temperature changes by direct immersion in water and liquid nitrogen respectively; six cycles.

3. As for (2), except upper cycle temperature raised to 100°C.

4.a Place in furnace at 400°C.

b. Quench in ice water.

c. Quench in liquid nitrogen.

d. Return to furnace at 400°C.

a to d -- six cycles.

5. Heat localized area of deposit (~ 1 cm diameter) with oxyacetylene torch while spraying opposing area on substrate with cold water.

6. Heat localized area of deposit (~ 0.5 cm diameter) with heliarc torch (9 volts, 40 amps) while spraying opposing area on substrate with cold water.

of the pure ceramic layer, both of which minimize the stress resulting from temperature changes or induced temperature gradients.

Microstructure and Composition

The microstructure of the yttria stabilized zirconia nickel coating is shown in Figure 4, together with the composition gradient through the thickness as measured by x-ray fluorescence. The grain structure is columnar with a typical diameter of 0.4 micron. A slight increase in diameter occurs from the substrate to the outer surface of the deposit. The nickel and zirconium composition traces superimposed on the micrograph are strongly nonlinear. Since the sputtering target was stepwise linear, a similar deposit profile, with some smoothing of the steps, was expected. The observed gradient can be accounted for on the basis of replenishment of nickel to the target surface by diffusion on the surface of zirconia particles. This replenishment would maintain a high concentration of nickel in the deposit until the nickel in the target was consumed. This behavior is generally prevented by cooling the target to reduce diffusion rates. Due to the insulating nature of the lowest layer of the target (i.e. pure ceramic) that was not possible in the present work.

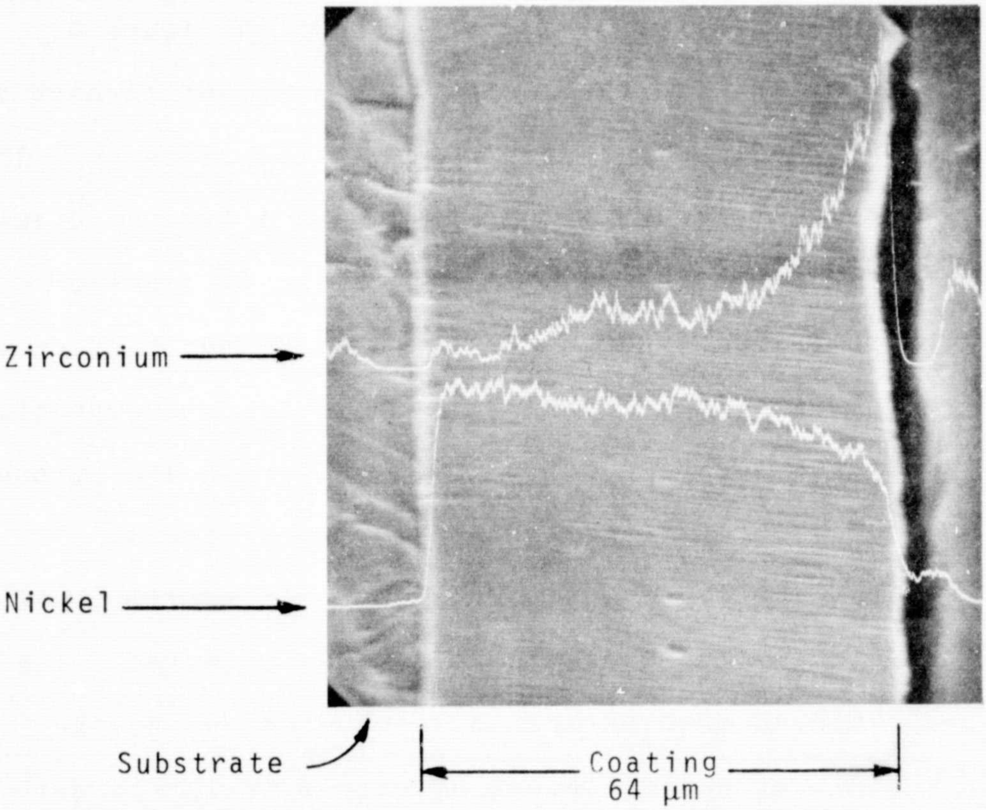


FIGURE 4. Microstructure and Composition Gradient of Deposit 8. Scanning Electron Micrograph.

Residual Stress

Attempts to measure the residual stress in the deposits by sectioning the rings and measuring the gap opening indicated low stress levels. For example, the gap resulting from cutting a coated ring was approximately equal to that resulting from cutting an uncoated ring.

Thermal Conductivity

A heat transfer apparatus was set up to measure the thermal conductivity of the coatings. The coated substrate was used as the divider between a central electrically heated water bath and an outer water bath heated via conductance through the specimen. The temperature difference between the baths was measured with a differential thermocouple. It was found that the thermal impedance of the two boundary layers was an order of magnitude greater than the thermal impedance of the specimen, therefore, effective measurements could not be made. Efforts to improve this situation, e.g. by use of liquid metals or radiation in vacuum, were considered beyond the scope of this contract.

TASK II

Coating of Spool Pieces for Firing Tests

Selection of the ceramic materials for this task could not be based on Task I work, since the results of

the screening tests were similar for the four materials investigated. Cost and time considerations indicated the use of alumina and magnesium-zirconate, since graded targets of these materials were available from Task I. This selection was also considered favorable from the standpoint of maximizing the difference between the two materials in terms of physical properties.

The spool pieces were lightly bead blasted to remove residual machining marks, which were thought to be more severe stress raisers than the unpatterned roughness produced by the bead blasting. They were rinsed with alcohol and immediately assembled into the apparatus.

The coating parameters were similar to those of depositions 7-10 (see discussion of Task I), with the exception that the approach to the pure ceramic was more complete. This was the result of using the actual yield data from previous runs rather than estimates. Also, the oxygen partial pressure was introduced earlier and taken to higher final values, again on the basis of the earlier experience. Together these factors account for the high resistance data shown in Table I.

The coatings were smooth, adherent and free of visible defects. A coated spool piece is shown in Figure 5. They were shipped to NASA LeRC 6-28-76.

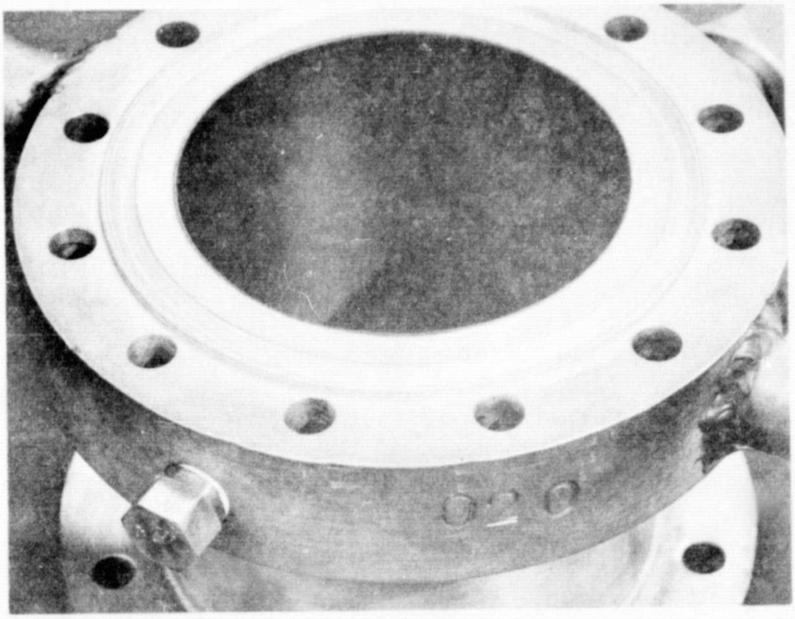


FIGURE 5. NASA Spool Piece after Deposition of Graded Nickel-Alumina Coating.

SUMMARY AND CONCLUSIONS

Graded composition deposits of nickel and various ceramics were produced by rf sputtering from plasma sprayed targets. The conditions found to produce adherent, insulating coatings were:

1) Low substrate temperature (< $100^{\circ}C$).
2) Decreasing rf power and increasing oxygen partial pressure with time as the material being sputtered approached pure ceramic.

The thermal cycling and shock tests used did not provide a basis for discriminating between the ceramics investigated, since all deposits remained adherent through all tests.

In discussions with the NASA program manager, magnesium zirconate and alumina were selected as the materials to be used for Task II coatings. The two required spool pieces and a third one intended for BNW test purposes, were successfully coated and shipped to NASA LeRC for firing tests.

RECOMMENDATIONS FOR FUTURE WORK

First priority in this program was given to adherence of the coatings. Thus the thickness of the pure ceramic portion of the coating was kept small. This decreases the effect of the coating in insulating the copper wall of the spool piece. If these coatings remain adherent through the firing tests, thicker ceramic layers should be investigated.

ACKNOWLEDGMENT

The authors wish to acknowledge technical assistance of the members of Materials and Process Engineering Section of BNW in accomplishing this work. The compositional and structural data were obtained by personnel in the Metallurgy Research Section.